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mmobilization of caesium-loaded ion exchange resins in zeolite-cement blends

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g of caesium (Cs)-loaded cemented ion exchange resin and the mechanism of Cs immobilization were studied in the ce- (mainly clinoptilolite) system. Present work focuses on the reduction of significant Cs leaching (in terms of the total Cs resin) by blending natural untreated and chemically treated zeolites to the cement. Addition of natural zeolites decreased Cs 70–75% (of the quantity originally bonded in the resin) in the course of a 3-year leaching period. © 1999 Elsevier Science served.

ctive waste; Transport properties; Admixture; Stability

countries, low-level radioactive waste immo- tegies are based on cementitious materials [1]. exchange resins from the primary cooling ssurized water reactor systems are favourably disposal. Heavy metals readily precipitate in environment of cements, but alkali metals, such (Cs) 137 (^{137}Cs), remain substantially soluble. ementation of Cs-loaded resins does have its Cs accumulates in the resin during operation of ut Cs-loaded resins, when cemented, show one of magnitude higher leach rates than the resins

of the high leaching of Cs from a preliminary ted samples in comparison with that from unce- loaded resins, our objective was to develop a rial that can significantly reduce this leachabil- ply with this aim, admixing zeolite seemed to be solution, as zeolites are present in large quanti- gary. Thus, release of Cs from specimens pre- g natural zeolite as well as various chemically ms was investigated. The optimum composition -zeolite ratio) was determined by strength mea- capacity and selectivity studies of zeolites, and ge resins. The migration of ions in the solid phase was assessed by diffusion experiments with cements and cements blended with zeolite.

1. Experimental

1.1. Materials and their performances

1.1.1. Solutions

In practice, performance lifetimes for waste forms are usually determined with reference to the ^{137}Cs isotope ($t_{1/2}$ = 30 years). In the present study, the shorter half-life isotope, ^{134}Cs, was used instead ($t_{1/2}$ = 2.05 years). CsCl solutions in various chemical and radiochemical concentrations, which contained the active isotope ^{134}Cs, were used for the saturation of ion exchange resins, the distribution and selectivity measurements, and the leaching tests. All determinations of Cs were carried out by radioisotope tracer techniques, except for the Cs-containing inactive solutions equilibrated with resins and zeolites, for which flame emission spectroscopy was used instead. Activities of the liquids were detected by a scintillation detector equipped with a NaI (Tl) cluster crystal.

1.1.2. Cement

For preparation of specimens to be used in leaching experiments, a 350-10 coded ordinary Portland cement (OPC) containing 10% pulverized fuel ash was used. The chemical composition of the cement is given in Table 1. The Cs adsorption potential of hardened cement paste and Cs distribution ratios between solid and solution phases, calculated us-

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Table 1
Chemical and mineralogical composition of cement and zeolite tuff (percent by weight)

Components	Chemical composition of cement* (%)	Chemical composition of zeolite tuff (%)
SiO_2	24.19	72.69
Al_2O_3	4.87	12.67
K_2O	0.65	3.32
CaO	58.23	2.23
Fe_2O_3	5.19	1.28
MgO	2.64	0.89
Na_2O	0.44	0.28
TiO_2	0.26	0.07
SO_3	1.96	n/d
Ign. loss	1.31	6.14
Total	99.74	99.57

Mineralogical composition of zeolite tuff	
Clinoptilolite	50%
K-feldspars	20%
Quartz	10%
Cristobalite	10%
Volcanic glass	10%

* Hungarian standard CEM II/A-V 32.5 R: produced at Beremend Cement Works.

ing Eq. (1), are listed in Table 2 (for test conditions, see Table 2 footnote).

$$R_d = \frac{(Cs^+)}{[Cs^+]} \tag{1}$$

where parentheses indicate concentration in the solid phase (mg/g), and square brackets indicate concentration in the liquid phase (mg/L).

1.1.3. Zeolite

The zeolite used originates from the Tokaj Hills deposit in Hungary. Table 1 lists the mineralogical composition, assessed by X-ray diffraction, X-ray fluorescence spectrometry (XRFS), and morphological studies, as well as the chemical composition of tuff. The 0.5- to 1.0-mm fraction of the zeolite tuff was used for sample preparation. Because ion exchange properties are altered on replacing the mobile ion in the zeolite [2], the ground mineral was pretreated by various methods (Na^+ form (1) [3]; NH_4^+ and H^+ form [4]; Na^+ form (2) [5]) to obtain different exchangeable cation contents.

Characterisation of one natural and four modif was performed by a radioisotopic method; their b and saturation capacities were determined by a dyna (Table 3). The Cs adsorption potential of untreated Cs distribution ratios between solid and solution given in Table 4 (for test conditions, see Table 4 f

Of the four variously treated zeolites, the hyd showed inferior ion exchange capacity and selecti natural zeolite; therefore, the H^+-form zeolite wa from subsequent cement addition experiments. A the unsatisfactory behaviour may be that, by having of its crystal water content, significant changes oc the zeolite structure [6].

1.1.4. Organic ion exchange resin

In the course of leaching studies, for the prepara specimens, a high-purity, styrene-based ion exchange (VARION KS-N) was used. This resin, in combinatio VARION AT-N resin, is also used for the water cle system of the Nuclear Power Plant Paks in Hungary. S tion of the pretreated resins was done by a static meth which a known quantity of the resin to be saturated is tacted for prolonged time (1 week) with a known concen tion of saturating solution (solution-to-resin volume ra 2.08). The advantage of the method is that it results in re beads of nearly similar saturation. In the course of the 1-we saturation period, the Cs solution contacting the resin w shaken several times every day. The quantity of Cs io bonded in the resin was determined from the difference of the signal frequencies (cps) of 1-mL samples taken before and after the saturation procedure. The saturation data of ion exchange resins used for leach sample preparation are listed in Table 5. The Cs adsorption potential of ion exchange resin and Cs distribution ratios between solid and solution phases are listed in Table 6 (for test conditions, see Table 6 footnote).

1.1.5. Selectivity measurement of ion exchange resin for Cs^+-Ca^{2+}

Selectivity ratios of ion exchange resins for Cs^+-Ca^{2+} were determined by following a static method. Quantities of 10-10 mL E(c) resin, termed saturated resin, were weighed into airtight polythene vessels and contacted with 100 mL $Ca(OH)_2$ solutions of different Ca^{2+} concentrations. Equilibration was accelerated by shaking the sealed vessels for 2 weeks. After this, 1-mL samples each were taken from the

Table 2
Caesium distribution ratios between hardened cement pastes and saturating solutions of different caesium concentrations*

Cs concentration of saturating solution (mg/L)	Cs concentration of solution after contacting (mg/L)	Cs concentration of cement paste after contacting (mg/g)	Distribution ratios (R_d) (mL/g)
1	0.671	0.0163	24.34
10	9.025	0.0483	5.34
100	98.96	0.0511	0.52

* Hydration time: 28 days, w/c = 0.35, hydration at room temperature, grain size of ground hydrated cement <200 mm, mass of hydrated cement: 0.5 g, volume of saturating solution: 25 ML, time of contacting: 2 weeks.

...ration capacities of zeolites*

	Break-through capacity (mg/g)	Saturation capacity (mg/g)
	40.00	69.51
	68.05	107.92
	101.14	139.15
	145.53	151.91
	164.54	189.79

... 10 × 100 mm, mass of zeolite: 6.3 g, Cs concentra-...ion: 0.1 mol/L, flow rate: 6 BV/h.

Table 5
Caesium saturation of ion exchange resins used

Resin	Saturation of resin (mol/L)	Resin	Saturation of resin (mol/L)
A(u)	0.612	A(c)	0.350
B(u)	0.725	B(c)	0.378
C(u)	0.807	C(c)	0.629
D(u)	0.949	D(c)	0.708
E(u)	1.164	E(c)	0.807

c: cemented, u: uncemented.

...olution and the $Ca(OH)_2$ solutions. Signal ...hese samples were determined. By knowing ...egree of ion exchange resin samples, the sig-...of a 1-mL sample of known concentration ...solution, from which solution samples for ...purposes were previously taken, the differ-...signal frequencies (cps) and the quantity of ... by the $Ca(OH)_2$ solutions one can calculate ...ios using Eq. (2). Calcium concentrations ...ned by titrimetry before and after $[Ca^{2+}]$ phase ...by the difference of which one could calculate ...ation of Ca on the resin (Ca^{2+}). Values of R_s ...atio) are listed in Table 7. Eq. (2) (see Table 7 ...definitions) refers to the exchange of Cs^+ and ...nd gives selectivity ratios for Ca^{2+}: the more ...ed in the resin, the higher the value of R_s.

$$\ldots \frac{\ldots(Ca^{2+})}{\ldots] \cdot (Cs^{+})} \quad (2)$$

...aration of leach test samples

...ere three series of leaching tests performed in this ...first series comprised uncemented resin samples, the ...vestigated cemented samples, and the third series ...d the behaviour of resins in zeolite-cement blends. ...ess the leaching character of uncemented resins, ...ples, previously saturated to various degrees [A(u) ...were placed in perforated polythene-walled vessels ...de and 4.4 mm high (70-mL volume), which were ...with a lid [7]. For the second series of leach tests, ...mples were first saturated to the required degrees ...E(c)] and then cemented by mixing 24 mL of resin, 93.2 g of cement, and ion-free water to achieve a paste of water-to-cement ratio of 0.3. For the third series, the suitable cement-to-zeolite ratio was selected by considering the results of strength tests [8], i.e., the highest zeolite content still ensuring sufficient strength was chosen. From compressive and tensile strength tests, as well as the water-to-solid ratios, a zeolite-to-cement ratio of 40/60 (by weight) was found to be the optimum. The zeolite-containing samples (coded as Natural B, Na(1)B, NHB, and Na(2)B according to the sort of zeolite contained) were prepared by mixing 24 mL of resin [A(c)], 55.9 g of cement, 37.3 g of zeolite, and ion-free water to achieve a paste of water-to-cement ratio of 0.3. Additionally, there was a reference sample (B) prepared containing no zeolite, thus being similar in composition to the samples of the second test series.

1.1.7. Leach tests

In the course of the leach tests, specimens were stored in 1-L volume, airtight PVC vessels that were filled with 750 mL of ion-free water and covered with a lid. The perforated ring on the bottom of the specimens and the size of the vessels ensured that the samples were surrounded with at least 20 mm of water on each side. The leach tests were done without renewal of the leachant; that is, the sampled leachants were returned to the vessel after measurement. The equipment used is illustrated in Fig. 1. During the first week of investigation, samples were taken daily, for the next month weekly, then at longer periods. The activities of the sample solutions (500 mL each time) were measured in a Marinelli vessel.

From the CsCl stock solution previously used for making solutions to saturate the resins, a standard solution of 10^{-3}

...distribution ratios between untreated zeolite and saturating solutions of different caesium concentrations*

...tration of ... solution	Cs concentration of solution after contacting (mg/L)	Cs concentration of zeolite after contaction (mg/g)	Distribution ratios (R_d) (mL/g)
	0.78	0.917	1175.7
	6.44	9.353	1450.9
	401	59.89	149.35
	9156	84.01	9.17

...olume of saturating solution: 100 mL, mass of zeolite: 1 g, grain size 0.5–1.0 mm, contacting time: 2 weeks.

Table 6
Caesium distribution ratios between organic ion exchange resins and different caesium concentration saturating solutions*

Cs concentration of saturating solution (mg/L)	Cs concentration of solution after contaction (mg/L)	Cs concentration of resin after contaction (mg/L)	Distribution ratio (mL/g)
10	0.5	3,167	$6.33 \times 10^{[illegible]}$
100	7.5	30,830	4.11×10^4
1,000	586.2	137,933	2.35×10^3
10,000	9,584.4	138,520	1.45×10^2

* Volume of saturating solution: 100 mL, volume of organic ion exchange resin: 0.3 mL, time of phase contacting: 2 weeks.

Table 7
Results of the Cs^+-Ca^{2+} selectivity determinations for the ion exchange resin

Sample	Ca^{2+} concentration in solutions before contacting (mol/L)	$[Cs^+]$ (mol/L)	$[Ca^{2+}]$ (mol/l)	(Cs^+) (mol/L resin)	(Ca^{2+}) (mol/L resin)	Cs^+-Ca^{2+} ratios (R_s)
R1	1.51×10^{-3}	1.53×10^{-3}	—	7.92×10^{-1}	1.51×10^{-2}	—
R2	1.76×10^{-3}	1.13×10^{-2}	—	6.95×10^{-1}	1.76×10^{-2}	—
R3	2.14×10^{-3}	3.00×10^{-2}	8.70×10^{-5}	5.07×10^{-1}	2.05×10^{-2}	13.96
R4	2.39×10^{-3}	4.38×10^{-2}	9.30×10^{-5}	3.70×10^{-1}	2.30×10^{-2}	[illegible]
R5	6.05×10^{-3}	6.08×10^{-2}	1.26×10^{-4}	1.99×10^{-1}	5.92×10^{-2}	[illegible]

Note: For Cs^+ and Ca^{2+} concentrations, parentheses indicate concentration in the resin phase and square brackets indicate concentration in the phase.

mol/L concentration was prepared by dilution. Signal frequency (activity) of this solution was determined before and after each series of measurements. This was done for two reasons; first, to compensate for probable instabilities of the measuring system, and second, to determine the absolute Cs concentrations of the leachates by taking the actual activity of a standard solution as reference (Figs. 2–4).

2. Results and discussion

On comparing leaching of Cs from uncemented and cemented ion exchange resins (first and second series), it can be seen that Cs concentrations of leachates are more than one order of magnitude higher for the second series samples. Considering the effect of increasing saturation degrees of the resins, the amount of leached Cs decreases for the cemented resin. In a cementitious environment, however, increasing the resin saturation, the amount of leached Cs [illegible]creases (Fig. 5). Removal of Cs from the uncemented [illegible] is low, not exceeding 0.06–0.88% of the initially bon[illegible] ions. As a consequence of cementation, these values cha[illegible] between 6.4–41.6%, depending on the saturation degree [illegible] the resin (Table 8).

Due to Ca^{2+} ions liberated during hydration reactions [illegible] well as readily soluble Na^+ and K^+, Cs^+ ions bonded on the resin are washed out to a significant degree (Table 7, R_1–R_5 1.9%, 14.0%, 37.2%, 54.3%, and 75.3%, respectively, [illegible] the initially bonded quantities, depending on the concentration within the resin). The Cs retention capacity of the cement-resin system on its own is rather low, as is that of OPC

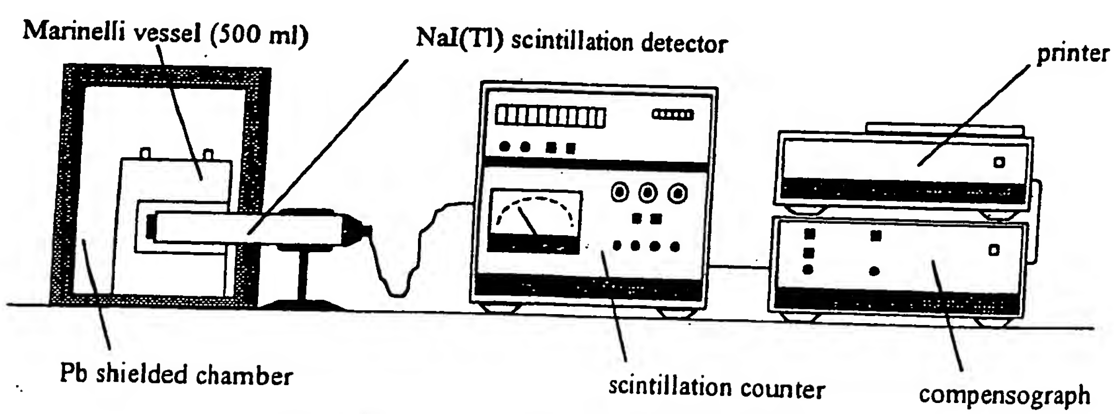

Fig. 1. Measuring system used to detect activities of leachates.

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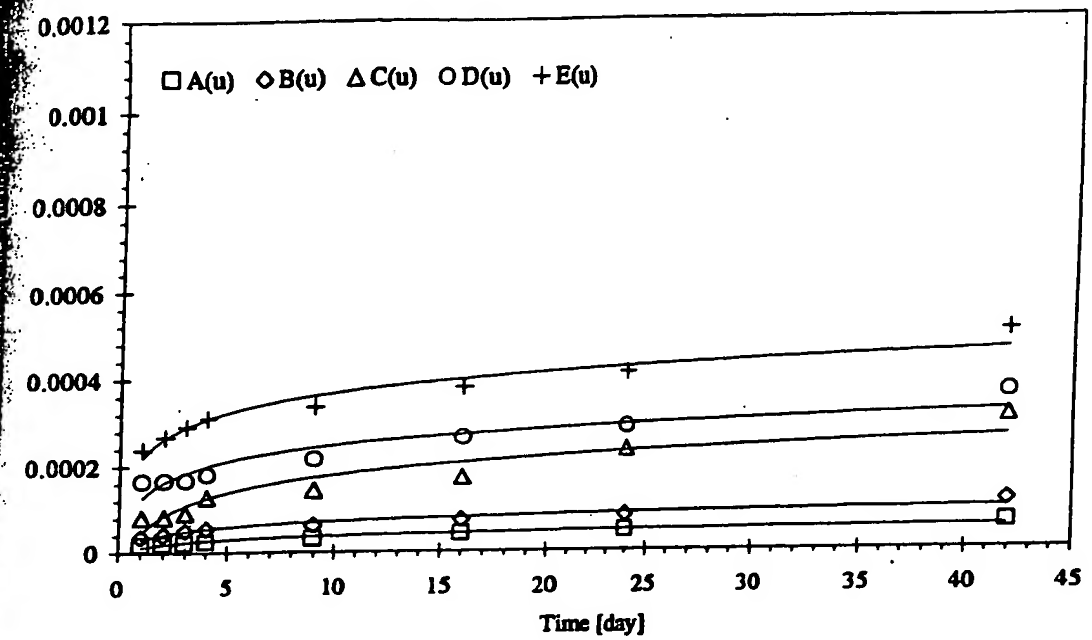

Fig. 2. Time dependence of caesium (Cs) concentration of leachates for uncemented ion exchange resin samples (first series).

...to suppress leaching, i.e., to lower the relatively ...concentration within the pore fluid of the cement ...menting resins, the third series of samples was pre... ...ixing cement, resin, and zeolite in selected com... The connection between the three constituents, ...porous, is established by the pore fluid that per... ...system. Therefore, the overall behaviour of the ...dependent on several equilibration processes (ion ... sorption, hydration etc.). Zeolites, especially those containing clinoptilolite, show excellent Cs retention (Table 4), which can be improved further by simple chemical treatments.

In the third series, the saturation degree of the resin was set to a relatively low value to simulate conditions in nuclear power plants, where, for operational safety reasons, ion exchange columns of the water treatment system are allowed to saturate to a moderate degree only.

On examining leaching for more than 3 years, the cemented resin containing no zeolite lost 70.4% of its origi-

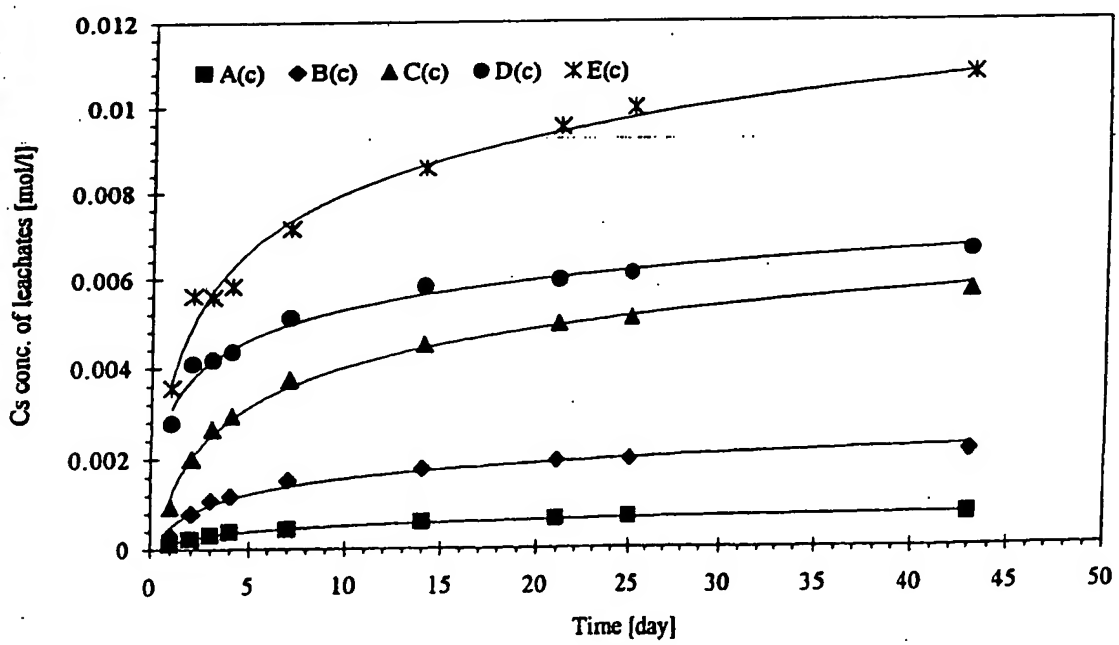

Fig. 3. Time dependence of the caesium (Cs) concentration of leachates in time for cemented ion exchange resin samples (second series).

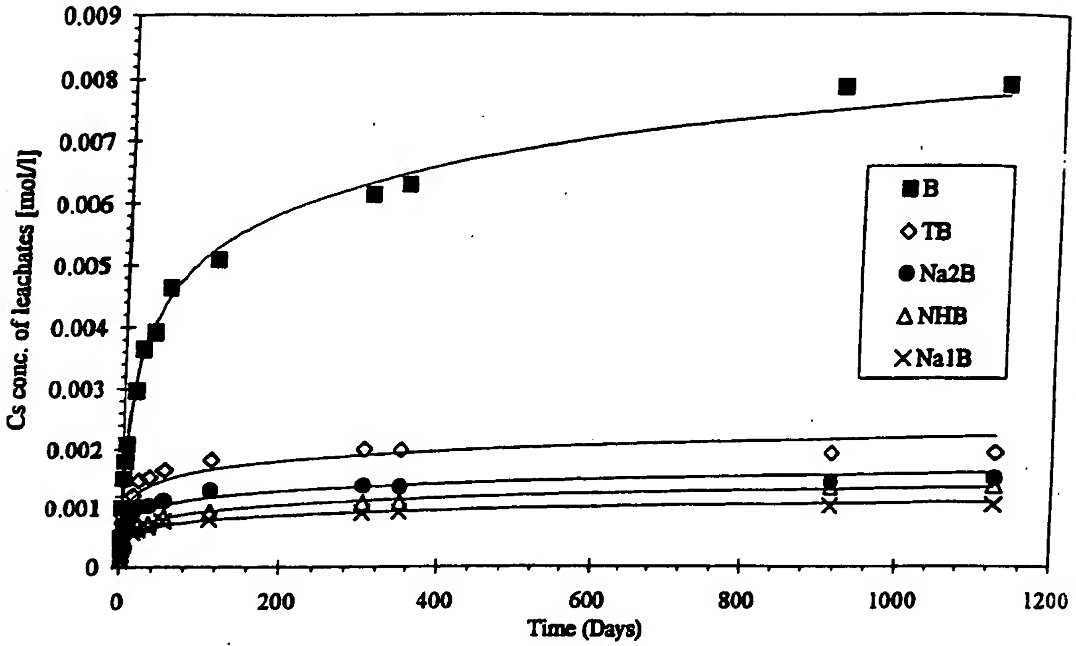

Fig. 4. Time dependence of the caesium (Cs) concentration of leachates in time for zeolite admixed cemented ion exchange resin samples (third series).

nally bonded Cs content (Table 8). Nevertheless, the major part of the Cs was removed within the first 100 days of leaching. With the presence of natural zeolite in the matrix, the amounts leached decreased to ~25%. With previous treatment of the zeolite to obtain Na^+ or NH_4^+ forms, further decreases in Cs leachability can be achieved. In the last 2 years of leaching, the increase of Cs concentration of the leachates is least for the zeolite containing samples.

3. Conclusions

The oldest and most often used technique for stabiliza-tion/solidification of radioactive wastes, cementation, is not satisfactory for immobilizing Cs-containing spent resins.

For suppressing the leachability of confined Cs, the cement-zeolite matrix gives better performance than does plain OPC.

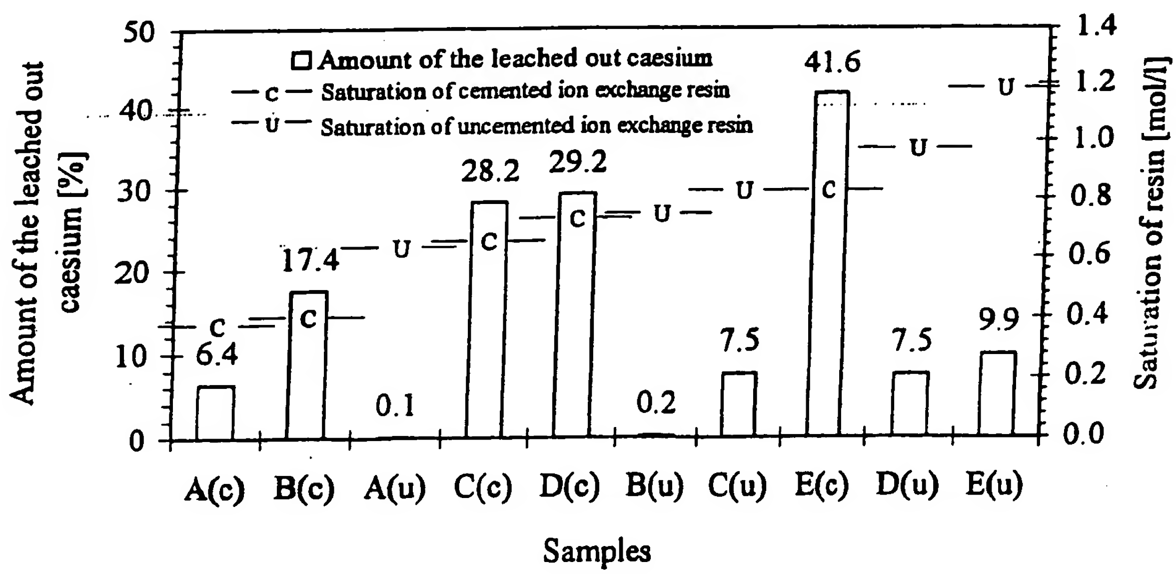

Fig. 5. Comparison of leach behaviour of cemented and uncemented organic ion exchange resin samples. Change of caesium concentration of leachates as a function of resin saturation after 40 days.

...) of caesium between resin and liquid phases as well as exclusion of caesium from ion exchange resins in percentage of the original

		Second series			Third series		
R_d	(%)	Sign of samples	R_d	(%)	Sign of samples	R_d	(%)
1207	0.88	A(c)	454.9	6.4	B	1.3	70.4
1986	0.54	B(c)	147.9	17.4	Natural B	14.9	17.3
2610	0.41	C(c)	79.5	28.2	Na(1)B	20.4	13.3
8478	0.13	D(c)	75.9	29.2	NHB	22.5	12.2
18947	0.06	E(c)	43.8	41.6	Na(2)B	30.4	9.3

...olites to the backfill between the solidified ... in underground repositories could further ...fety of disposal.

...ments

... are indebted to the Commission of the Euro... ...ities for their financial support (COST-PECO ...IPDCT 930447).

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